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<b>(21) International Application Number:</b> PCT/BE98/00146 <b>(22) International Filing Date:</b> 5 October 1998 (05.10.98) <b>(30) Priority Data:</b> 9721812.7                      15 October 1997 (15.10.97)                      GB <b>(71) Applicant (for all designated States except US):</b> GLAVERBEL [BE/BE]; Chaussée de la Hulpe 166, B-1170 Brussels (BE). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GOELFF, Pierre [BE/BE]; Rue Grand Douze Bois 31, B-6120 Nalinnes (BE). DE- GAND, Etienne [BE/BE]; Bosweg 31, B-1970 Wezem- beek-Oppem (BE). <b>(74) Agent:</b> VANDENBERGHEN, Lucienne; Glaverbel, Dept. Industrial Property, Centre R. & D., Rue de l'Aurore 2, B-6040 Jumet (BE).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> TRANSPARENT HEAT-SWELLABLE MATERIAL  <b>(57) Abstract</b>  A transparent heat-swellaable material, a method for its preparation and fire-resistant glazing panels in which it is incorporated, are provided by a mixture of hydrated alkali metal silicate and an additive selected from polyalcohols and mono- or polysaccharides, in which the additive content is in the range of 5 to 22 % by weight, the water content is in the range of 12 to 19.5 % by weight, and the hydrated alkali metal silicate has a silicon oxide (SiO <sub>2</sub> ): alkali metal oxide molar ratio greater than 3.3 to 1. Glazing panels including the said material offer thermal insulation of greater than 30 minutes, a barrier to flames and fumes for greater than 90 minutes and thermal radiation of less than 10 kW/m <sup>2</sup> , or even of less than 6 kW/m <sup>2</sup> , after 90 minutes.		

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### **Transparent heat-swellaable material.**

This invention relates to a transparent heat-swellaable material and to a fire-resistant glazing panel having multiple layers of glazing material with the said heat-swellaable material bonded thereto.

The general requirements for a fire-resistant panel are to provide  
5 an effective barrier against flames and fumes and to provide thermal insulation. When all other parameters are constant, the extent of the fire resistance may depend on the type and size of glazing, the type of materials used in its construction and the manner in which it is held in a surrounding frame in an aperture. While glass is non-combustible it may itself soften or break under  
10 intense heat from a fire, or its frame may burn or distort, such that the barrier fails and direct fire propagation or escape of fumes can occur.

The use of a transparent heat-swellaable material between layers of glazing material to improve the fire-resistant properties of glazing panels is well established, to enhance the resistance of the panel both to heating in  
15 general and to exposure to fire in particular. The panel is formed as a laminate with a layer or layers of the transparent heat-swellaable material each sandwiched between two transparent structural plies, usually thin glass sheets.

GB patent 1590837 teaches the use of an intumescent material sandwiched between two structural plies in a laminated fire screening panel. It  
20 describes the use of hydrated metal salts as the intumescent material, especially hydrated alkali metal silicates such as hydrated sodium silicate. Later proposals have been concerned with modifying the silicate to improve its fire-resisting properties. For example WO94/04355 describes and claims a protective layer comprising a cured polysilicate prepared from an alkali metal silicate and a  
25 curing agent. EP-A-0705685 relates to a fire-resistant glazing panel comprising at least two glass sheets and an intermediate layer mainly composed of sodium water glass (sodium silicate) and water, together with hydrated potassium silicate and a small proportion of polyalcohols or sugars.

During the course of a fire, the silicate material slowly swells as  
30 the temperature increases, the water of hydration is driven off by the heat of the fire, and the material is converted to a foam which serves as a barrier to both radiated and conducted heat and may also preserve the ability to bond

together structural sheets of the panel such as sheets of glass which may become shattered by the fire.

Panels are typically graded according to the length of time of heating under defined conditions until failure occurs in respect of such properties as insulation and integrity. In the initial period of a fire, up to about 30 minutes, the panel should provide a high level of thermal insulation in order to facilitate the escape or if necessary the rescue of people in the affected area. This period is normally sufficient to permit the safe exit of everyone other than the fire-fighters who remain to control and extinguish the fire. The panel should also have sufficient integrity to provide a barrier to flame and fumes and a restraint to radiation of heat for at least the first 30 minutes and preferably for at least 60 minutes. With increasing emphasis on safety provisions in the home and at the workplace there is an increasing demand for panels to offer longer periods both of integrity, for example of 90 minutes or more, and of low radiation. Such longer periods are seen as important in seeking to provide sufficient time for fire-fighters to remain in a building and to control and extinguish the fire with minimum loss and damage to the affected property.

The fire-resistance of glazing panels is tested by mounting them in a wall of a furnace whose interior temperature is then increased according to a pre-determined schedule. Such a test is specified in International Standard ISO 834-1975 and is also described in International Standard ISO 9051-1990 which speaks specifically of the fire-resistance requirements for glazed assemblies. Similar European standards are proposed, including draft standard prEN1363 (document CEN/TC127 N 1095) and draft standard prEN1364 (document CEN/TC127 N 1085).

Draft standard prEN1363 includes a "Cotton wool pad" test and a "Gap gauge" test. In the former a cotton wool pad in a frame is placed for a maximum of 30 seconds adjacent to an area of a test glazing specimen under examination for failure of integrity. The time and location at which any ignition of the pad occurs are recorded. In the latter a 6 mm gap gauge and a 25 mm gap gauge are in turn applied without undue force to determine (a) whether the 6 mm gauge can be passed through a gap in the specimen into the furnace and moved 150 mm along the gap and (b) whether the 25 mm gauge can be passed through a gap in the specimen into the furnace.

It is an objective of the present invention to provide a transparent heat-swellable material which offers for fire-resistant glazing panels a period of heat insulation and an extended period of fire-resistance, especially in terms of its "integrity", i.e. providing a barrier to flame and fumes, and of

restrained radiation of heat. These features should moreover be provided without making the panel cumbersome and heavy.

According to this invention, there is provided a transparent heat-swella-  
ble material comprising hydrated alkali metal silicate and at least one  
5 additive selected from polyalcohols and mono- or polysaccharides,  
characterised in that the additive content is in the range 5 to 22% by weight,  
the water content is in the range 12 to 19.5% by weight, and the hydrated  
alkali metal silicate has a silicon oxide ( $\text{SiO}_2$ ):alkali metal oxide molar ratio  
greater than 3.3 to 1.

10 The invention further includes within its scope a sheet of  
transparent vitreous material carrying a layer of the above-defined heat-  
swella-ble material, and a fire-resistant panel comprising one or more layers of  
the said heat-swella-ble material and a corresponding two or more sheets of  
transparent vitreous material.

15 The term "heat-swella-ble" used herein refers to materials,  
otherwise known as intumescent materials, with the properties, when exposed  
to a flame, of swelling and forming an insulating barrier to propagation of the  
flame.

The heat-swella-ble silicate materials of the invention offer  
20 considerable improvements in the thermal insulation, integrity (barrier to flame  
and fumes), and thermal radiation of glazing panels formed from them. The  
reasons for these improvements are not entirely clear but probably result from  
the combination of the claimed additive and an unusually low proportion of  
water. Another important factor appears to be that the silicates with a  
25  $\text{SiO}_2$ :alkali oxide molar ratio of greater than 3.3:1 expand less during standard  
fire tests than known materials obtained by drying alkaline silicate sols with a  
molar ratio of up to 3.3:1. The reduction in thermal radiation appears to result  
in part from the good integrity of the panel and the very low rates of flow of the  
foams arising from heat-swella-ble material according to the invention upon  
30 their exposure to fire.

The improvements are especially surprising in the case of soda-  
lime glass sheets which are commonly used in laminated glazing since the  
transformation temperature of the glass remains very largely below the  
temperatures reached during the fire tests; the transformation temperature of  
35 the foams in themselves is again largely less than that of the soda-lime glass.

The preferred alkali metal silicate is sodium silicate with a  
 $\text{SiO}_2$ : $\text{Na}_2\text{O}$  molar ratio of about 4:1. A combination of this preferred silicate  
with a silicate having a lower  $\text{SiO}_2$ : $\text{Na}_2\text{O}$  molar ratio, such as 3.3:1, also

provides a panel with beneficial fire-resistant properties, provided that the total  $\text{SiO}_2\text{:Na}_2\text{O}$  molar ratio is greater than 3.3:1.

Preferred examples of the additive are glycerol, ethylene glycol and saccharose. It is typically to be employed in an amount of 5 to 21% by weight of the transparent heat-swella-  
5 ble material. Glycerol is the most preferred additive. It is preferably employed in an amount of 10 to 16% by weight of the transparent heat-swella-  
ble material.

The water content of the said material should be in the range 12 to 19.5 %, typically 12 to 19 %, by weight. The preferred range is 15 to 19.5%  
10 by weight.

In one preferred embodiment the invention provides a transparent heat-swella-  
ble material comprising hydrated sodium silicate and glycerol, characterised in that the glycerol content is in the range 5 to 20% by weight, the water content is in the range 14 to 19% by weight, and the  
15 hydrated sodium silicate has a silicon oxide ( $\text{SiO}_2$ ):sodium oxide ( $\text{Na}_2\text{O}$ ) molar ratio greater than 3.3 to 1.

The panels according to the invention preferably include at least two layers of the said material and at least three layers of transparent vitreous material. A particularly preferred panel configuration comprises three layers of  
20 the said material and four layers of the transparent vitreous material.

As mentioned above, the transparent vitreous material is most typically soda-lime float glass and the present invention is primarily described with reference thereto. Other types of vitreous material, for example borosilicate or aluminosilicate glass or of vitro-ceramic material, may however  
25 be employed for particular purposes, such as low expansion glass, extra-clear glass, hardened, armoured or coated glass. Usual plastics materials tend to be unsuitable for fire-resistant panels since they may ignite and may generate toxic fumes.

Panels according to the invention may be incorporated in double  
30 glazing and/or associated with polymer sheets or films. They may include a combination of thin and thick sheets of the transparent vitreous material. A thickness of less than 5 mm is preferred for each sheet of vitreous material in order to provide a panel which is thin, light and easy to install into a window or door frame.

35 The transparent heat-swella-  
ble material of the invention is preferably formed from a starting solution of hydrated alkali metal silicate and an additive. Care should be taken when preparing the starting solution to avoid agitation which would cause air or other gas to dissolve since these could

reappear as microbubbles at a later stage. The solution is then partially dried to form a viscous material, known as a "solid gel".

Thus the present invention further provides a method for the preparation of a transparent heat-swellaable material from a starting solution of hydrated alkali metal silicate and at least one additive characterised in that the  
5 hydrated alkali metal silicate has a silicon oxide ( $\text{SiO}_2$ ):alkali metal oxide molar ratio of greater than 3.3 to 1, the additive is selected from polyalcohols and mono- or polysaccharides, and the solution is partially dried to form a solid gel having a content in the range 5 to 22% by weight, and a water content in the  
10 range 12 to 19.5% by weight.

In a preferred embodiment of the method of the present invention the starting solution is dried in such a way that the silicate product is in the form of grains. To form a glazing panel from this preferred granular form of the material, the grains are evenly distributed as a layer on a surface of a  
15 vitreous sheet. A second vitreous sheet is then placed on the grains, followed by further grain layers and sheets if required.

The maximum dimension of the grains is preferably in the range 10 to 700  $\mu\text{m}$ , most preferably in the range 150 to 500  $\mu\text{m}$ . These sizes facilitate formation of the grains into a compact layer with good optical and  
20 fire-resistance properties. Their beneficial effect on the behaviour of the silicate layer during the course of a fire may possibly be the result of their achieving a fine and uniform foam structure when subjected to the intense heat of the fire.

Instead of converting the starting solution to granular form before application to the vitreous sheet, the solution can be applied directly to  
25 the sheet and then dried *in situ* thereon. The starting solution is highly viscous and its viscosity is increased by the drying, thereby assisting in keeping it in place.

The so-assembled panel is subjected to heat and pressure conditions to cause the silicate layer, whether formed from grains or directly  
30 from the solution, to bond to the respective adjacent surfaces of the vitreous sheets. The temperature for this stage is preferably at least 80°C and the applied internal pressure initially less than 30 kPa, as described in GB patent specification 2258422. In the case of a granular layer, the heat and pressure convert the grains into a continuous layer in which individual grains are not  
35 visible to the naked eye: the layer presents a uniform transparent appearance.

The heat and pressure also serve to degas the silicate product, thereby preventing the occurrence of visible gas micro-bubbles at or near the surface of the applied layer, which would otherwise adversely affect the optical

properties of the layer and thus of the panel.

The panel is then subjected to further heating and pressure, typically in an autoclave, to complete the bonding.

To avoid bonding to the resulting silicate layer of any moulding plate used to compact the granular layer during assembly of a panel, the plate may be treated in an appropriate manner, for example with a silicone. In one convenient embodiment of the invention the moulding plate is constituted by, or faced with, a sheet which is to become incorporated into the panel and to which the silicate layer becomes bonded. The or each silicate layer may thus be sandwiched between two sheets of the panel which is simultaneously formed into a laminate by the heat and pressure treatment employed for the bonding. Indeed the whole panel may be assembled and formed into a laminate by that treatment.

The thickness of the or each layer of silicate material is preferably in the range 0.1 to 5.0 mm. While layers as thin as 0.1 mm can give adequate short-term protection against fire, better protection is afforded by thicker layers. In general, increasing the thickness of such a layer beyond 5 mm does not give a commensurate increase in the degree of protection afforded and creates difficulties in achieving good optical properties.

In one embodiment of the invention the starting material includes an anti-ageing agent in an amount of up to 2% by weight. Preferably the anti-ageing agent is a quaternary ammonium compound, most preferably tetramethyl ammonium hydroxide (TMAH). The anti-ageing agent retards the ageing properties of the heat-swellaible material which tend to occur as deterioration of the optical properties of the panel, for example a reduction in the transparency of the silicate.

The invention thus offers fire-resistant panels having for example the following advantageous features in regard to the standards required of such panels:

- a small (less than 20 mm) total panel thickness;
- thermal insulation of greater than 30 minutes;
- integrity (barrier to flames and fumes) of greater than 90 minutes; and a ratio of integrity to thermal insulation of more than 2;
- thermal radiation of less than 10 kW/m<sup>2</sup>, or even of less than 6 kW/m<sup>2</sup>, after 90 minutes.

The combination of thermal insulation of greater than 30 minutes and thermal radiation of less than 10 kW/m<sup>2</sup> after 90 minutes is a particularly advantageous feature of the invention.



The invention is further described in the following non-limiting examples.

#### Example 1

The starting materials for the example were sodium silicate  
5 solution, glycerol and tetramethyl ammonium hydroxide (25% aqueous solution). The silicate had a dry sodium silicate content of 28.9% by weight and a density of 1.276 at 20°C. Its silicon oxide:sodium oxide molar ratio was 4.04. The glycerol was of 99% purity.

To 100 litres of the silicate solution were added 7 litres of the  
10 glycerol and 3 litres of the TMAH solution, forming 110 litres of a silicate starting solution. The so-formed starting solution was partially dehydrated on a drum dryer, yielding a fine granular powder with a glycerol content of about 15.6% by weight, a water content of about 17.0% by weight, a TMAH content of 1.3% by weight and a particle size of less than 700  $\mu\text{m}$ .

15 A laminated transparent glazing panel with an alternate succession of 4 sheets of soda-lime float glass and of 3 layers of transparent silicate was formed from the silicate grains and sheets of soda-lime float glass of 3 mm thickness and measuring 1.5 x 2.8 m. The glass sheets were first cleaned in a washing machine and dried. Powder was then deposited on a horizontally  
20 disposed glass sheet to a uniform thickness and in an amount of 2.2 kg/m<sup>2</sup>. A second glass sheet was then placed on the deposited grains. Further grains were deposited on the second glass sheet, again uniformly in an amount of 2.2 kg/m<sup>2</sup>. Third and fourth glass sheets were similarly added, with similar intervening grains deposited uniformly in an amount of 2.2 kg/m<sup>2</sup>. The so-  
25 formed multi-ply panel assembly of sheets and silicate layers was compacted under reduced pressure of about 13 kPa (absolute) while its temperature was slowly raised from ambient (20°C) to about 100°C. The pressure was allowed to return to atmospheric and the panel was then placed for 3 hours in an autoclave heated to 130°C and submitted to a pressure of 13000 hPa, thereby  
30 completing the bonding.

Each silicate layer in the finished panel had a thickness of 1.2 mm and the total thickness of the panel was 15.6 mm. The finished panel was cut to dimensions of 1.0 m x 2.0 m, with samples of 200 mm x 200 mm being also taken.

35 Two similar panels measuring 1.0 m x 2.0 m were mounted in a frame as described in French patent specification 2593223. The frame was itself held within a masonry surround measuring 3.0 x 3.0 m. The masonry surround was then fitted into a corresponding opening in the wall of a gas

furnace. The ambient temperature was 15°C. The furnace was heated according to the heating curve defined in the draft standard prEN 1363. The panel was subjected to standard tests for thermal insulation (mean and local, according to draft standard prEN 1364), integrity (using both the "cotton wool pad" test and the "gap gauge" tests of draft standard prEN1363) and for the thermal radiation emitted after 90 minutes at 1 metre from the centre of the panel along a normal thereto, using a heat flux transducer (Medtherm Corporation Series 64). The results are shown in the accompanying table.

Two of the 200 mm x 200 mm samples were placed for 30 days in a thermal chamber held at 80°C. Their optical qualities remained substantially unchanged, with haze remaining below 1%.

#### Example 2

The procedure of Example 1 was repeated, except for changes in the composition of the silicate starting solution and for the use of a larger panel (1.2 m x 2.7 m). The starting solution was formed of 100 litres of silicate and 9 litres of glycerol. It was employed to form a silicate layer of 1.2 mm thickness. The contents of glycerol and water in the layer material were respectively 19.8% and 15.1% by weight.

The resulting panel had a thickness of 15.6 mm. It was subjected to the above-described standard tests for thermal insulation, integrity and thermal radiation. The results are shown in the accompanying table.

The panel was placed in a chamber heated to 80°C and kept therein for 21 days. Its optical qualities remained substantially unchanged, with haze remaining below 1%.

#### Examples 3 and 4

The procedure of Example 1 was again adopted, except that the starting solution was formed of 100 litres of silicate, 5 litres of glycerol and 3 litres of TMAH solution and that the silicate with a silicon oxide:sodium oxide molar ratio of 4.04 was partially substituted (50% in Example 3, 25% in Example 4) by silicate with a silicon oxide:sodium oxide molar ratio of 3.3. The partially dehydrated product had contents of water, glycerol and TMAH of respectively 17.8%, 11.1% and 1.3% by weight in Example 3, and 17.2%, 11.7% and 1.4% by weight in Example 4. The panels (measuring 1.0 m x 2.0 m) were formed from three glass sheets and two silicate layers. They were subjected to the standard tests as the previous Examples. The results are shown in the accompanying table.

#### Example 5

In a variation of Example 1, a panel was formed according to the

general procedure described therein but with an additional glass sheet and an additional layer of silicate, making a total of 5 glass sheets and 4 silicate layers. The glass sheets each had an area of 1.2 x 2.7 metres and a thickness of 2.5 mm. The silicate again had a silicon oxide:sodium oxide molar ratio of 4.04. The silicate starting solution was formed of 100 litres of silicate, 7 litres of glycerol and 3 litres of TMAH solution, giving contents of water, glycerol and TMAH in the formed layer of 17.0%, 15.6% and 1.3% by weight.

The resulting panel had a thickness of 17.3 mm. It was subjected to the standard tests as in the previous Examples. The results are shown in the accompanying table.

#### Example 6

In a further variation of Example 1, the starting solution was formed of 100 litres of silicate ( $\text{SiO}_2:\text{Na}_2\text{O}$  4.04:1), 7 litres of glycerol and 0.4 litres of TMAH solution, giving contents of water, glycerol and TMAH in the formed layer of 16.8%, 15.9% and 0.2% by weight.

The formed panel had 4 sheets of soda-lime float glass of 3.2 mm thickness and 3 layers of the transparent silicate. It measured 1.2 x 2.7 m and had a total thickness of 16.4 mm. It was subjected to the standard tests as in the previous Examples and the results are shown in the accompanying table.

#### Example 7

In this example the starting materials were potassium silicate, glycerol, tetramethyl ammonium hydroxide (25% aqueous solution) and saccharose (800 g/l solution). The silicate had a dry potassium silicate content of 29.6% by weight and a density of 1.2615 at 20°C. Its silicon oxide:potassium oxide molar ratio was 4.07. The glycerol was of 99% purity.

To 68.9 litres of the silicate solution were added 8.1 litres of the glycerol, 2.08 litres of the TMAH solution, and 0.7 litres of the saccharose solution. Part of the so-formed solution was applied as a coating of uniform thickness to two horizontally disposed sheets of soda-lime float glass each measuring 1.0 m x 2.0 m and having a thickness of 2.85 mm. The amount of the solution applied to the glass was 3.3 l/m<sup>2</sup>. The so-coated sheets were placed in a heated chamber with a relative humidity of 85% in which the temperature was progressively raised to 90°C to effect partial dehydration of the coating and were then laminated with a third sheet of soda-lime float glass to form a glazing panel having a total thickness of 10.95 mm. The resultant silicate layers in the panel had a glycerol content of about 22.0% by weight, a water content of 19.2% by weight, a TMAH content of 1.1% by weight and a saccharose

content of 1.2%.

The panel was subjected to the standard tests as in the previous examples. The results are shown in the accompanying table.

#### Example 8

5 The procedure of Example 1 was repeated, except that the starting solution was formed of 100 litres of sodium silicate, 8 litres of glycerol and 0.4 litres of TMAH. The partially dehydrated product had contents of water, glycerol and TMAH of respectively about 16.0%, 17.9% and 0.2% by weight.

10 The resulting panel was formed from three sheets of borosilicate float glass measuring 1.2 x 2.0 m with a thickness of 3.3 mm. It was subjected to the standard tests as in the previous examples. The results are shown in the accompanying table.

#### Example 9

15 The procedure of Example 1 was repeated, except that the starting solution was formed of 90 litres of sodium silicate, 10 litres of potassium silicate (of the same composition as in Example 7), 7 litres of glycerol and 0.4 litres of TMAH. The partially dehydrated product had contents of water, glycerol and TMAH of respectively about 18.2%, 15.6% and 0.2% by weight.

20 The resulting panel was formed from four sheets of soda-lime float glass measuring 1.2 x 2.0 m with a thickness of 3.1 mm. It was subjected to the standard tests as in the previous examples. The results are shown in the accompanying table.

#### Example 10

25 The procedure of Example 8 was repeated. The partially dehydrated product again had contents of water, glycerol and TMAH of respectively about 16.0%, 17.9% and 0.2% by weight. In this example however the glass employed for the three sheets of the panel had the following composition (by weight):  $\text{Al}_2\text{O}_3$  7.7%;  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  9.9%;  $\text{BaO} + \text{SrO} + \text{CaO} + \text{MgO}$  20%;  $\text{ZrO}_2$  2.5%; and  $\text{SiO}_2$  59%. The sheets had a thickness of 2.8 mm and the silicate layers had a thickness of 1.2 mm.

30 The panel, which measured 1.0 x 1.0 m, was subjected to the standard tests as in the previous examples. The results are shown in the accompanying table.

TABLE

Ex.	% of 4.0Si:Na silicate	Layer thickness	Thermal insulation		Integrity		Therm. radn. after 90 min (kW/m <sup>2</sup> )
			Mean	Local	Cotton	Gap gauge	
		(mm)	(min)	(min)	(min)	(min)	
1	100	1.2	33	37	105	115	5
2	100	1.2	36	43	>105	>105	NM
3	50	1.2	24	27	67	>69	7 <sup>1</sup>
4	75	1.2	21	26	100	100	5 <sup>1</sup>
5	100	1.2	54	57	85	>98	NM
6	100	1.2	39	42	78	95	NM
7	100 <sup>2</sup>	1.2	20	17	55	84	NM
8	100	1.3	23	25	147	150	6
9	90 <sup>3</sup>	1.2	33	35	51	92	7
10	100	1.2	22	23	NM	162	6

NM = not measured

1 = measured at 60 minutes

2 = 100 % **potassium** silicate

3 = 90 % sodium silicate + 10 % **potassium** silicate.

## CLAIMS

1. A transparent heat-swellaable material comprising hydrated alkali metal silicate and at least one additive selected from polyalcohols and mono- or polysaccharides, characterised in that the additive content is in the range 5 to 22% by weight, the water content is in the range 12 to 19.5% by weight, and the hydrated alkali metal silicate has a silicon oxide ( $\text{SiO}_2$ ):alkali metal oxide molar ratio greater than 3.3 to 1.
2. A material as claimed in claim 1, in which the hydrated silicate is sodium silicate ( $\text{Na}_2\text{O}$ ).
3. A material as claimed in claim 2, in which the sodium silicate has a  $\text{SiO}_2$ : $\text{Na}_2\text{O}$  molar ratio of about 4:1.
4. A material as claimed in claim 1 or claim 2, which includes a combination of hydrated sodium silicate with a  $\text{SiO}_2$ :( $\text{Na}_2\text{O}$ ) molar ratio of about 4:1 and a hydrated sodium silicate having a  $\text{SiO}_2$ : $\text{Na}_2\text{O}$  molar ratio in the range 3.3:1 to 4:1.
5. A material as claimed in any preceding claim, in which the additive content is in the range 5 to 21% by weight.
6. A material as claimed in any preceding claim, in which the additive is glycerol.
7. A material as claimed in claim 6, in which the glycerol content is in the range 10 to 16% by weight.
8. A material as claimed in any preceding claim, in which the water content is in the range 12 to 19% by weight.
9. A material as claimed in any of claims 1 to 7, in which the water content is in the range 15 to 19.5% by weight.
10. A transparent aqueous heat-swellaable material comprising hydrated sodium silicate and glycerol, characterised in that the glycerol content is in the range 5 to 20% by weight, the water content is in the range 14 to 19% by weight, and the hydrated sodium silicate has a silicon oxide ( $\text{SiO}_2$ ):sodium oxide ( $\text{Na}_2\text{O}$ ) molar ratio greater than 3.3 to 1.
11. A material as claimed in any preceding claim, which further includes an anti-ageing agent in an amount of up to 2% by weight.
12. A material as claimed in claim 11, in which the anti-ageing agent is tetramethyl ammonium hydroxide (TMAH).
13. A method for the preparation of a transparent heat-swellaable material from a starting solution of hydrated alkali metal silicate and at least

one additive, characterised in that the hydrated alkali metal silicate has a silicon oxide ( $\text{SiO}_2$ ):alkali metal oxide molar ratio of greater than 3.3 to 1, the additive is selected from polyalcohols and mono- or polysaccharides, and the solution is partially dried to form a solid gel having a content in the range 5 to 22% by weight, and a water content in the range 12 to 19.5% by weight.

14. A method as claimed in claim 13, in which the starting solution is dried in such a way as to form grains.

15. A method as claimed in claim 14, in which the maximum dimension of the grains is in the range 10 to 700  $\mu\text{m}$ .

16. A method as claimed in claim 15, in which the maximum dimension of the grains is in the range 150 to 500  $\mu\text{m}$ .

17. A method of forming a transparent glazing panel, in which a gel prepared according to claim 13 is evenly distributed as a layer on a surface of a vitreous sheet and is subjected to heat and pressure to bond the layer to the vitreous sheet.

18. A method of forming a transparent glazing panel, in which grains prepared according to claim 14 are evenly distributed as a layer on a surface of a vitreous sheet and are subjected to heat and pressure to bond the layer to the vitreous sheet.

19. A method as claimed in claim 17 or claim 18, in which the bonding is effected at a temperature of at least 80°C.

20. A method as claimed in any of claims 17 to 19, in which the or each of the said layers is sandwiched between two sheets of the panel which is formed into a laminate at the same time as the or each layer is subjected to heat and pressure.

21. A sheet of transparent vitreous material carrying a layer of material as claimed in any of claims 1 to 12.

22. A fire-resistant panel comprising one or more layers of material as claimed in any of claims 1 to 12 and a corresponding two or more sheets of transparent vitreous material.

23. A fire-resistant panel as claimed in claim 22, which includes three layers of the defined silicate material and four layers of the transparent vitreous material.

24. A fire-resistant panel as claimed in claim 22 or claim 23, in which the sheets of transparent vitreous material have a thickness of less than 5 mm.

25. A fire-resistant panel as claimed in any of claims 22 to 24, in which the or each layer of silicate material has a thickness in the range 0.1 to 5.0 mm.

26. A fire-resistant panel as claimed in any of claims 22 to 25,  
5 having a thickness of less than 20 mm.

27. A fire-resistant panel as claimed in any of claims 22 to 26, having when exposed to fire a thermal insulation of greater than 30 minutes.

28. A fire-resistant panel as claimed in any of claims 22 to 27, providing when exposed to fire an integrity of greater than 90 minutes.

10 29. A fire-resistant panel as claimed in any of claims 22 to 28, having a ratio of integrity to thermal insulation of more than 2.

30. A fire-resistant panel as claimed in any of claims 22 to 29, having when exposed to fire thermal radiation of less than  $10 \text{ kW/m}^2$  after 90 minutes.

15 31. A fire-resistant panel as claimed in claim 30, having thermal radiation of less than  $6 \text{ kW/m}^2$  after 90 minutes.

32. A fire-resistant panel as claimed in any of claims 22 to 30, having when exposed to fire the combination of thermal insulation of greater than 30 minutes and thermal radiation of less than  $10 \text{ kW/m}^2$  after 90 minutes.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 98/00146

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C09K21/02 B32B17/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 705 685 A (FLACHGLAS AG) 10 April 1996 cited in the application see the whole document ---	1-32
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 225 (C-189), 6 October 1983 & JP 58 120548 A (ASAHI GLASS KK), 18 July 1983 see abstract ---	1-32
A	US 4 873 146 A (GOELFF PIERRE ET AL) 10 October 1989 see examples 1,2 ---	1-32
A	US 4 190 698 A (BAUDIN POL ET AL) 26 February 1980 see examples 1,2 ---	1-32
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

7 December 1998

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 98/00146

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	<p>US 4 720 414 A (BURGA ROQUE F)</p> <p>19 January 1988</p> <p>see column 3, line 18 - line 50</p> <p>-----</p>	1-32

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